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Specification

(54) [Title of Invention] A Method for Manufacturing
Carbonic Esters

(57) [Summary]

[Purpose] To efficiently obtain carbonic esters from carbon dioxide and alcohol while preventing loss of catalytic activity by removing the water produced as the reaction proceeds.

[Composition] A dehydrating agent is added to the reaction system before carrying out the reaction in order to remove the water produced as the reaction proceeds. Examples of dehydrating agents used include orthoformate triesters, orthoacetate triesters, dicyclohexylcarbodiimide, molecular sieves, cyclopropanone, and chloral.

[Effect] By adding a dehydrating agent, the life of the catalyst is markedly improved compared to reactions in which such agents are not added, thus providing an industrially outstanding method for manufacturing carbonic esters.

[Claims]

[Claim 1] Method for manufacturing carbonic esters, characterized in that, in manufacturing carbonic esters by reacting alcohol and carbon dioxide in the presence of a catalyst composed of metal compounds, a dehydrating agent is added to the reaction system, and the reaction is carried out while removing the water that is produced.

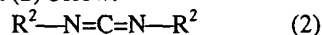
[Claim 2] Manufacturing method according to Claim 1, characterized in that the dehydrating agent is a compound having General Formula (1) below:



(in the formula, R denotes hydrogen or an alkyl or aryl group, and R^1 denotes an alkyl or aryl group).

[Claim 3] Manufacturing method according to Claim 1, characterized in that the dehydrating agent is a molecular sieve.

[Claim 4] Manufacturing method according to Claim 1, characterized in that the dehydrating agent is a compound having General Formula (2) below:



(in the formula, R^2 denotes an alkyl, cycloalkyl, or aryl group).

[Claim 5] Manufacturing method according to Claim 1, characterized in that the dehydrating agent is cyclopropanone.

[Claim 6] Manufacturing method according to Claim 1, characterized in that the dehydrating agent is chloral.

[Detailed Description of the Invention]

[0001]

[Fields of Industrial Use] The present invention concerns a method for manufacturing carbonic esters by reacting alcohol and carbon dioxide. Carbonic esters are useful as raw materials for manufacturing products such as alkylating agents, carbonylating agents, solvents, gasoline additives, agricultural chemicals, pharmaceuticals, polycarbonate, etc.

[0002]

[Prior Art] In the past, it was possible to manufacture carbonic esters by various methods. For example, the method of reacting phosgene and alcohol and synthesizing carbonic esters accompanying dehydrochlorination is widely known. In this method, however, the highly toxic substance phosgene is used as a raw material, and caution is required in handling this substance. Moreover, extensive investments in equipment are required in order to maintain safety, thus increasing costs.

[0003] Other examples of known synthesis methods include the method of reacting carbon monoxide and alcohol with oxygen in the presence of a metal catalyst, and synthesizing carbonic esters as dehydration proceeds. For example, a method using a copper compound as a catalyst is presented in Japanese Unexamined Patent Application No. S45-11129, which describes a method in which carbon monoxide, alcohol, and oxygen are reacted in the presence of cupric ions such as cupric chloride and cupric bromide. Moreover, Japanese Examined Patent Application Publication S60-58739 presents a method in which carbon monoxide, alcohol, and oxygen are reacted using bromide, chloride, or a monovalent copper salt such as cuprous perchlorate as a catalyst. The drawbacks of these methods include the fact that as carbonic ester production activity is low, the amount of the copper compound used is great; the fact that large amounts of catalytic components precipitate because of

low solubility, making special equipment necessary for carrying out the reaction and recovering and recycling the catalyst; the fact that large amounts of alkyl halides, esters, etc., are produced as byproducts; and the fact that carbon monoxide is oxidized to form carbon dioxide. Japanese Unexamined Patent Application No. H1-279859 presents a method in which, the water content in the reaction solution is controlled to 3% or less in order to improve catalytic stability, as copper catalysts readily lose their activity on contact with water.

[0004] Moreover, methods are widely known in which alcohol and carbon dioxide are reacted in order to synthesize carbonic esters. Japanese Examined Patent Application Publication No. S56-40707 presents a method for synthesizing carbonic esters by reacting alcohol and carbon dioxide in the presence of a tin alkoxide or titanium alkoxide catalyst. In this method, however, the catalyst is inactivated by water released during the course of the reaction, resulting in insufficient turnover.

[0005]

[Problems to be Solved by the Invention] The aforementioned methods in which carbon monoxide, alcohol, and oxygen are reacted in the presence of a copper catalyst to synthesize carbonic esters have drawbacks such as the fact that carbon monoxide is relatively expensive and highly toxic, the fact that as the reaction is carried out in the presence of oxygen, it is difficult to inhibit the production of oxidation byproducts, and the fact that the decrease in catalytic activity due to the release of water cannot be prevented.

[0006] Moreover, in methods in which carbon dioxide and alcohol are reacted in the presence of a tin or titanium catalyst in order to synthesize carbonic esters, although many problems connected with the synthesis of carbonic esters from carbon monoxide, alcohol, and oxygen are resolved because relatively inexpensive carbon dioxide is used and oxygen is not present in the reaction system, the problem of inactivation of the catalyst due to released water remains unsolved.

[0007] The purpose of the present invention is to provide a method for advantageously manufacturing carbonic esters, characterized in that in synthesis of carbonic esters using inexpensive carbon dioxide as a raw material, catalytic inactivation is prevented and catalytic turnover is maintained at a sufficient level.

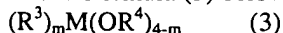
[0008]

[Means for Solving Problems] The following is a detailed explanation of the present invention. The inventors of the present invention conducted extensive research on methods for synthesizing carbonic esters from carbon dioxide and alcohol using metal alkoxy compounds as catalysts in which released water was removed in order to prevent catalytic inactivation, and as a result, they discovered that by adding a dehydrating agent to the reaction system, released water can be quickly removed and catalytic activity can be maintained over long periods, thus arriving at the present invention.

[0009] Specifically, the present invention concerns a method for manufacturing carbonic esters by reacting alcohol and carbon dioxide in the presence of a catalyst composed of metal compounds, characterized in that a dehydrating agent is

added to the reaction system in order to remove the water produced during the reaction.

[0010] The catalyst used in the present invention is a compound having General Formula (3) below



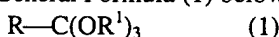
(in the formula, R^3 and R^4 denote alkyl or aryl groups, m denotes an integer from 0 to 3, and M denotes a metal), or a compound having General Formula (4) below



(in the formula, R^5 denotes an alkyl or aryl group and M denotes a metal). Examples of R^3 , R^4 , and R^5 include methyl, ethyl, *n*-propyl, *i*-propyl, *n*-butyl, phenyl, tolyl, and anisyl groups. Examples of M include Sn and Ti.

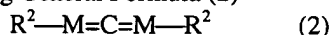
[0011] Examples of raw material alcohols that can be used in the present invention include aliphatic alcohols such as methanol, ethanol, propanol, and butanol, unsaturated alcohols such as allyl alcohol, and aromatic alcohols such as phenol, but aliphatic alcohols, particularly methanol, are preferred.

[0012] The dehydrating agent of the present invention is a compound having General Formula (1) below



(in the formula, R denotes a hydrogen or an aryl or allyl group, and R^1 denotes an alkyl or aryl group), with examples including orthoformate and orthoacetate esters.

[0013] Moreover, the dehydrating agent may also be a compound having General Formula (2)



(in the formula, R^2 denotes an alkyl, cycloalkyl, or aryl group), with examples including cyclohexylcarbodiimide. Moreover, the dehydrating agent may also be a molecular sieve, cyclopropanone, or chloral.

[0014] Either a single dehydrating agent or a combination of two or more such agents may be used. The partial pressure of carbon dioxide in the reaction system should be in the range of 1-250 kg/cm², and particularly 10-150 kg/cm². The reaction temperature should be in the range of 50-250°C, and preferably 100-200°C. If the reaction temperature is too low, the reaction rate will become slower, and if it is too high, decomposition of the carbonic ester produced will be stimulated, producing an undesirable result.

[0015]

[Working Examples] The following is an explanation of the present invention by means of working examples, but the scope of the invention is not limited to these examples.

[0016] Working Example 1

10 mL of methanol, 1.5 g of dibutyldimethoxy tin as a catalyst, and 8.8 g of trimethyl orthoformate as a dehydrating agent were placed in a 100 mL SUS autoclave equipped with an agitator, and after carbon dioxide was pumped in three times using a carbon dioxide pump in order to purge the interior of the autoclave, the internal pressure of the autoclave was adjusted to 30 kg/cm². After this, the autoclave was heated to 150°C under agitation, and the reaction was allowed to proceed for 24 hours. During the heating reaction, the internal pressure of the autoclave reached approximately 100 kg/cm². After cooling, the residual carbon dioxide was discharged, and the reaction

solution was analyzed by gas chromatography. The results confirmed that 5.9 g of dimethyl carbonate and 4.1 g of methyl formate had been produced. The molar ratio of the amount of dimethyl carbonate produced to the amount of catalyst added was 13.2, which means that the catalytic regeneration figure was 6.6.

[0017] Working Example 2

10 mL of methanol, 1.5 g of dibutyldimethoxy tin as a catalyst, and 10 g of trimethyl orthoacetate as a dehydrating agent were placed in a 100 mL SUS autoclave equipped with an agitator, and after carbon dioxide was pumped in three times using a carbon dioxide pump in order to purge the interior of the autoclave, the internal pressure of the autoclave was adjusted to 30 kg/cm². After this, the autoclave was heated to 150°C under agitation, and the reaction was allowed to proceed for 8 hours. During the heating reaction, the internal pressure of the autoclave reached approximately 100 kg/cm². After cooling, the residual carbon dioxide was discharged, and the reaction solution was analyzed by gas chromatography. The results confirmed that 2.2 g of dimethyl carbonate and 1.9 g of methyl acetate had been produced. The molar ratio of the amount of dimethyl carbonate produced to the amount of catalyst added was 5.0, which means that the catalytic regeneration figure was 2.5.

[0018] Working Example 3

10 mL of methanol, 1.5 g of dibutyldimethoxy tin as a catalyst, and 8.5 g of DCC (dicyclohexylcarbodiimide) as a dehydrating agent were placed in a 100 mL SUS autoclave equipped with an agitator, and after carbon dioxide was pumped in three times using a carbon dioxide pump in order to purge the interior of the autoclave, the internal pressure of the autoclave was adjusted to 30 kg/cm². After this, the autoclave was heated to 150°C under agitation, and the reaction was allowed to proceed for 8 hours. During the heating reaction, the internal pressure of the autoclave reached approximately 100 kg/cm². After cooling, the residual carbon dioxide was discharged, and the reaction solution was analyzed by gas chromatography. The results confirmed that 2.1 g of dimethyl carbonate had been produced. The molar ratio of the amount of dimethyl carbonate produced to the amount of catalyst added was 4.6, which means that the catalytic regeneration figure was 2.3.

[0019] Working Example 4

23 mL of butanol, 1.5 g of dibutyldimethoxy tin as a catalyst, and 8.5 g of DCC (dicyclohexylcarbodiimide) as a dehydrating agent were placed in a 100 mL SUS autoclave equipped with an agitator, and after carbon dioxide was pumped in three times using a carbon dioxide pump in order to purge the interior of the autoclave, the internal pressure of the autoclave was adjusted to 30 kg/cm². After this, the autoclave was heated to 150°C under agitation, and the reaction was allowed to proceed for 8 hours. During the heating reaction, the internal pressure of the autoclave reached approximately 100 kg/cm². After cooling, the residual carbon dioxide was discharged, and the reaction solution was analyzed by gas chromatography. The results confirmed that 4.1 g of dibutyl carbonate had been produced. The molar ratio of the amount of dibutyl carbonate

produced to the amount of catalyst added was 4.8, which means that the catalytic regeneration figure was 2.4.

[0020] Comparison Example

10 mL of methanol and 1.5 g of dibutyldimethoxy tin as a catalyst were placed in a 100 mL SUS autoclave equipped with an agitator, and carbon dioxide was pumped in three times via a carbon dioxide pump in order to purge the autoclave, after which its internal pressure was adjusted to 30 kg/cm². After this, the autoclave was heated to 150°C under agitation, and the reaction was allowed to proceed for 24 hours. The internal pressure of the autoclave during the heating reaction reached 100 kg/cm². After cooling, the residual carbon dioxide was discharged, and the

reaction solution was analyzed by gas chromatography. The results confirmed that 0.4 g of dimethyl carbonate had been produced. The molar ratio of the amount of dimethyl carbonate produced to the amount of catalyst added was 0.8, which means that the catalytic regeneration figure was 0.4.

[0021]

[Effect of the Invention] As explained above, the present invention provides an industrially outstanding method for manufacturing carbonic esters in which a dehydrating agent is added to the reaction system, thus sharply increasing catalytic turnover and markedly prolonging catalyst life.